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### Recommended Citation

A. G. Sedekar et al., "Photolithographically Patterned Covalently Bonded Polythiophene Films using in Tandem Sol-gel, Surface Initiated Free Radical and Redox Polymerization Methods," *Polymeric Materials: Science and Engineering*, American Chemical Society (ACS), Aug 2008.

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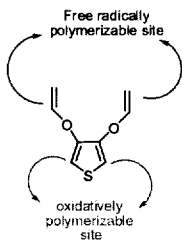
# Photolithographically Patterned Covalently Bonded Polythiophene Films Using In Tandem Sol-Gel, Surface Initiated Free Radical And Redox Polymerization Methods

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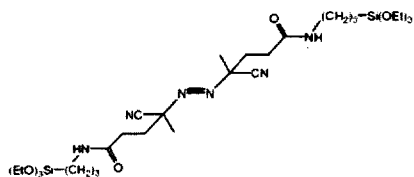
## INTRODUCTION

A bifunctional monomer, 3,4-bis(vinyloxy)thiophene (BVOT), that can be polymerized both by radical as well as by redox chemistry was utilized in the fabrication of lithographic patterns of conducting polymer films via a sol-gel method. The judicious use of several chemistries yields polythiophene patterns covalently bonded to substrate showing superior adhesion relative to physically bonded counterparts. The films were characterized electrically and mechanically.



BVOT

Surface confinement starts with a bidentate free radical initiator (Si-AIBN) synthesized via a condensation reaction between 3-aminopropyltriethoxysilane (APTES) and azobiscyano-valeric acid.<sup>1</sup> Si-AIBN is attached to the surface of glass by hydrolysis of the ethoxy groups and reaction with the hydroxyl groups on the glass surface.



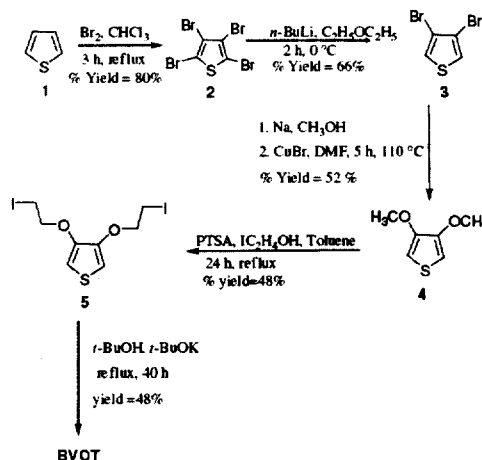
Si-AIBN

Subsequently, BVOT was free-radically polymerized via the vinyl groups by surface-bound Si-AIBN and was confined on the surface of glass. In turn, dangling thiophene groups can in principle be polymerized oxidatively. But, as the distance and spatial orientation of the thiophene groups is such that they cannot be polymerized by their own, they were bridged by oxidative copolymerization with EDOT. This unique film-making method offers the obvious advantage of excellent adhesion as compared to the physically bonded films. In addition, crosslinking offers excellent hardness and chemical stability. In a slight twist, films were successfully patterned photolithographically showing that patterns of any desired electrical circuit can be made easily.

## EXPERIMENTAL

**Materials.** Thiophene, bromine, methylene chloride and *t*-butanol were purchased from Acros and were used as received unless noted otherwise. Chloroform, *n*-butyllithium (2 M solution in hexane), anhydrous DMF, anhydrous methanol, 2-iodoethanol and potassium *t*-butoxide were used as received from Aldrich. Diethyl ether, sodium hydroxide, cuprous bromide, *p*-toluenesulfonic acid, toluene, sodium sulfate, and sodium bisulfite were purchased from Fisher Scientific. *t*-Butanol and diethyl ether were dried by refluxing over sodium metal (from Fluka) for 3 h followed by distillation. Cuprous bromide was dried in an oven at 200 °C for 12 h before use. Toluene was dried by refluxing over phosphorous pentoxide for 3 h followed by distillation. N<sub>2</sub> was obtained from BOC Gases, Murray Hill, N.J. supplied locally by Ozarc Gases.

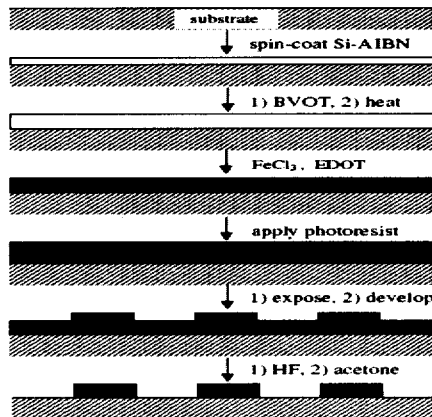
Scheme 1. Synthesis of BVOT.



**Methods.** BVOT was synthesized by modification of literature procedures as summarized in Scheme 1.<sup>2,3</sup>

**Preparation of Photolithographically Patterned Films.** (Scheme 2): Glass slides (2"×2") were cleaned by boiling for 2 min in Micro™ solution, washing with copious amounts of D.I. water and then boiling again in water for 2 min. Slides were bench-dried for 24 h. Si-AIBN initiator was applied on these slides by spin coating (1 min, 1500 rpm) a THF solution (0.1122 M) and dried in the dark for 24 h. Then BVOT was applied by brush over the initiator-coated glass slides, which were kept in an airtight glass container at 70 °C for 12 h.

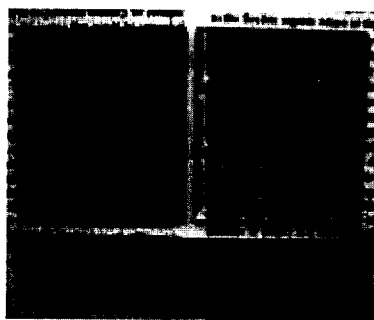
Scheme 2. Preparation and patterning of BVOT-EDOT films.



Unreacted BVOT was removed by dipping the film in  $\text{CH}_3\text{CN}$ . Subsequently, dry films were dipped in a 1 M  $\text{FeCl}_3$  solution in  $\text{CH}_3\text{CN}$ , and EDOT was added externally to make the  $\text{CH}_3\text{CN}$  solution 50 mM in EDOT concentration. The container was manually stirred and after 10 min, the glass slides were washed with  $\text{CH}_3\text{CN}$  and were ultrasonicated in  $\text{CH}_3\text{CN}$  for 1 min. To the above prepared blue BVOT-EDOT films, photoresist was applied by spin coating and baked for 1 h at 100 °C. Photoresist was exposed through a mask to the long wavelength of a hand-held UV source for 20 min. The exposed resist was developed leaving the desirable pattern on the BVOT-EDOT polymer film. Finally, BVOT-EDOT films coated with patterned resist were dipped in 10% HF solution for 8-10 s removing the resist unprotected blue film. The remaining photoresist was washed off with acetone, leaving behind a patterned covalently bonded conducting polymer film of BVOT-EDOT. Photolithography in similar manner does not form any pattern on plain glass, which confirms that the pattern was formed by etching off only the covalently bonded polymer film.

### RESULTS AND DISCUSSION

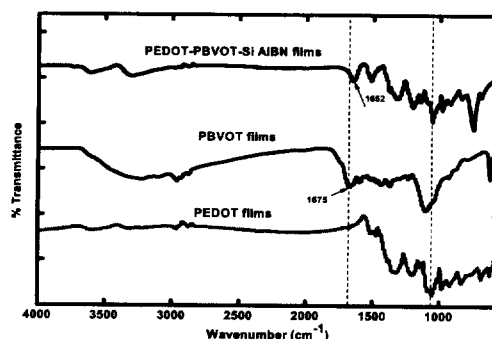
Typical films obtained by the process of Scheme 2 are shown in Figure 1.



**Figure 1.** BVOT-EDOT films obtained by the process of Scheme 1. Left: before photolithographic patterning. Right: after photolithographic patterning.

Control experiments prove that films are not produced by homopolymerization of EDOT, but rather EDOT acts as a bridging agent between dangling thiophene moieties from BVOT. Without surface initiated polymerization of BVOT, adherent blue films fail to form. The thickness of the blue composite films was measured using a Dektak II profilometer and it was found around 200 nm. The conductivity of the films was measured as  $65 \text{ S m}^{-1}$  using a Cascade CPS6 four probe conductivity meter, calibrated using a silicon wafer of known conductivity. The films were also characterized for adhesion (ASTM D3359-97), pencil hardness (ASTM D 3363-00), MEK rub resistance. The films pass 5B on adhesion scale very easily, the films also sustain 6H pencil hardness. After 40 MEK rubs the films still show conductivity.

Chemical characterization was conducted by IR. Homopolymer films of PBVOT and PEDOT were prepared by electropolymerization and the final films were prepared by the method of Scheme 2, scraped and IR spectra in KBr pellets were obtained. In PBVOT we observe the characteristic doublet peak ( $\text{C}=\text{C}$  stretch) of vinyl ethers at about  $1675 \text{ cm}^{-1}$ .



**Figure 2.** IR spectra of Homopolymers of PBVOT, PEDOT and films made by the process scheme 2.

This peak is not observed in PEDOT. In the PBVOT-PEDOT films made by the method of Scheme 2, the vinyl groups are polymerized by radical polymerization and are not found in the spectra. But there is a peak at  $1652 \text{ cm}^{-1}$  which is typical of carbonyl of amide ( $\text{O}=\text{C}-\text{NH}$ ) stretch coming from the free radical initiator.

### CONCLUSIONS

The covalently bonded conducting polymers serve as a new class of materials which exhibit enhanced mechanical strength over their physically bonded counterparts. This class of materials also gives freedom to make robust patterned films with the combination of surface initiated polymerization followed by redox chemistry.

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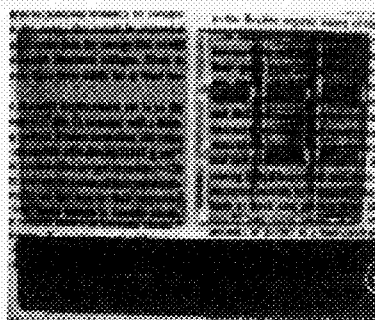


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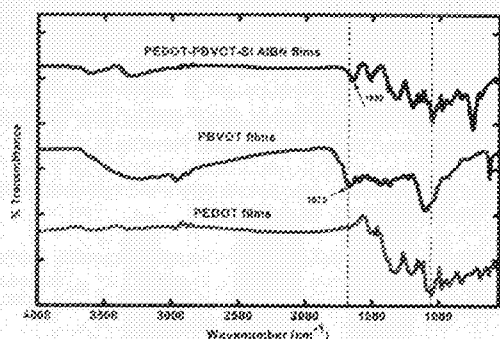


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